Lithium Isotopes in the Mono Basin Hydrologic System, Mono Lake, CA

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Introduction Because of significant mass fractionation during near-surface processes (Chan and Edmond, 1988; Huh et al., 1998), and the near absence of such effects during igneous processes (Chan et al., 1992; Tomascak et al., 1999), Li isotopes have the potential for revealing new information in hydrological settings. In order to realize this potential, it is necessary to make some detailed studies of natural systems, and to test resulting hypotheses with experiments. We are currently examining Li isotopes in hydrologically closed lake basins, focusing initially on Mono Lake, California, to better understand solute budgets. Mono Lake is located in eastern California, at the foot of the eastern Sierra Nevada, and receives most of its water from Sierran creeks. Additional sources are from both cold and warm springs near or in the lake. Mono Lake is highly saline and alkaline and has extremely high Li concentration (~10 ppm). In contrast it has exceedingly low Ca (and Sr) concentrations due to CaCO₃ supersaturation. isotopic compositions of Mono basin waters can be used as a robust fingerprint of the Sr sources to the lake (as demonstrated by Neumann and Dreiss, 1995), whereas Li isotopes more likely record some combination of source and mass dependent fractionation processes. Additionally, the contrasting residence times will lead to different sensitivities of the systems. The ultimate goal of this study is to investigate chemical change in the lake over time, as recorded by Li, B and Sr isotope compositions and rare earth element patterns of ostracodes and other chemical precipitates.

Geochemical Data Mono Lake water has 87 Sr/ 86 Sr of 0.7096, and δ^7 Li of +20. The δ^7 Li of meromictic Mono Lake has not changed over our three years of sampling, and the compositions above and below the chemocline are indistinguishable. Although creeks dominate its water budget, springs may be a significant source of solutes to the lake. For example, the Li concentration of thermal spring water is ~100x greater than average creek water. Creeks have 87 Sr/ 86 Sr of 0.7086 to 0.7100, but most spring samples are similar to lake Sr. Li isotopes in creek waters are rather variable (+11 to +29), with no apparent correlation between Li and Sr isotopes. Creek waters are very dilute with respect to Li. Given the δ^7 Li of the two principal permanent creeks (Rush and Lee Vining), we conclude that the predominant creek water isotopic signature is lighter than current lake water, in the range +12 to +15.

Thermal springs contribute water with 87 Sr/ 86 Sr as low as 0.7071, and δ^7 Li as low as +8.4. These values are similar to Quaternary volcanic rocks of the area, which have relatively low 87 Sr/ 86 Sr (up to 0.7065) and low δ^7 Li (+3.8). The Li isotope compositions measured for young volcanic and Sierran plutonic rocks in the Mono Basin are identical to normal mid-ocean ridge basalts, emphasizing the importance of surficial rather than high temperature processes in fractionating the isotopes of Li. These light compositions appear to typify Great Basin thermal waters, as hot springs at Pyramid Lake, NV, and in Long Valley show δ^7 Li from +3.0 to +11.9. This suggests

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that Mono basin thermal springs may derive their Li-Sr isotope characteristics from either equilibration with young volcanic rocks and their sediments or they may possess a significant magmatic water component.

Groundwater springs are also somewhat variable in 87 Sr/ 86 Sr, but the variability correlates well with δ^7 Li (from +7.4 and 0.7086 to +31 and 0.7099). The high 87 Sr/ 86 Sr is consistent with Sierran igneous and metamorphic sources, although these are not isotopically uniform. Although scant published analyses of Li isotopes in granitic crustal materials suggest heavier Li isotopic compositions (Bottomley et al., 1999), our analysis of a granodiorite from the Tuolumne intrusive suite suggest more mantle-like values (+3.6).

A single measurement of a direct carbonate precipitate from the lake shows only slight fractionation from the lake itself (+18). This indicates that carbonate precipitation probably is not a principal control on the Li isotopic composition of the lake.

The lithium isotope composition of efflorescent salts from the lake's eastern playa (+32) match the isotopically heavy values for some groundwater springs. We suggest that this signature is generated during water-sediment interaction, to some extent in the unsaturated zone. These sediments are principally volcanic debris and rock flour. However, even in the absence of clays, such reactions should drive fluid isotopic compositions to progressively heavier values (e.g., Huh et al., 1998; Zhang et al., 1998). Hence salts forming from their evaporation should carry this fractionation imprint. This interpretation needs to be tested, however, by analysis of sediments themselves, and can be further substantiated with experimental simulations.

Lithium Budget Simple mass balance modeling suggests that due to high Li concentrations, spring sources exert fundamental controls on the Li budget of the lake. Viewed collectively, the springs define a mixing field: one end member has high 87 Sr/ 86 Sr and 7 Li higher than lake water (groundwater springs), the other end member has low 87 Sr/ 86 Sr and low, mantle-like 7 Li (young volcanic rocks, thermal spring water) (Figure 1). This relation suggests that the principal influence on the Li isotopic composition of the modern lake is through mixing of these isotopically distinct sources, perhaps secondarily modified by fractionation. Given the higher concentration of Li in thermal waters compared to groundwater springs, mixing calculations indicate that groundwater springs must dominate the spring water contribution to the lake.

The budget considerations are made in two end member scenarios. The calculation uses the modern values of concentration and isotopic composition and assumes effects of post-mixing fractionation processes (e.g., during crystallization) are negligible. In the first case it is assumed that 85% of the water to the lake is contributed by Sierran creeks (Blevins et al., 1987). In this situation, the modern lake Li isotope composition can be reproduced using a volume ratio of 33:1 (groundwater:thermal springs) and indicates that creeks supply only 20% of lake Li. In the second case it is assumed that the creeks provide 93% of the Mono Lake water budget. In this situation, the creeks provide just under 40% of the Li to the lake. As the creeks supply Li that is isotopically lighter than lake water, the balance is preserved by increasing the ratio of groundwater to thermal springs to 46:1. One readily apparent result of these calculations is that small increases in thermal spring flux (e.g., during periods of heightened volcanic/seismic

activity) have the potential to strongly perturb the Li isotopic budget of the lake, and might have even larger influence on the Sr due to the shorter residence time.

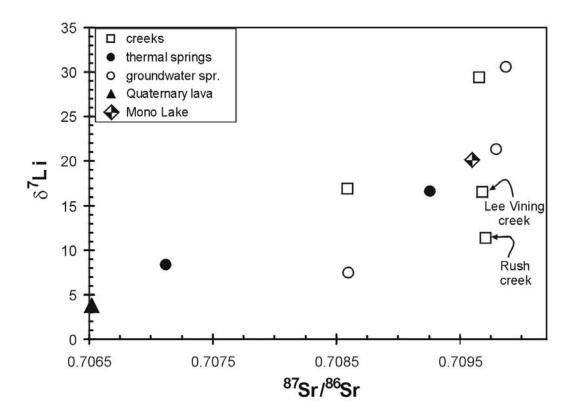


Figure 1. $\delta^7 \text{Li v.}^{87} \text{Sr/}^{86} \text{Sr}$ for Mono basin materials. Li isotope data are $\pm 1\%$.

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